

# Efficient Two-Step Synthesis of Biodiesel from Greases<sup>†</sup>

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Received June 19, 2007. Revised Manuscript Received September 27, 2007

Biodiesel (BD) is an alternative diesel fuel derived from both vegetable oils and animal fats. Currently, most BD is made by alkali-catalyzed transesterification of a refined oil or fat, the cost of which is the major expenditure in producing BD. Yellow and brown greases are readily available renewable fats that are less expensive and hence represent attractive feedstocks for the production of BD. The high free fatty acid (FFA) content of these feedstocks, however, makes it difficult to produce BD using base-catalyzed transesterification. In this paper, we report the use of a series of diarylammonium catalysts that are highly effective in catalyzing the esterification of the FFA present in greases (12–40 wt % FFA). At a catalyst loading of 2–3 mol %, high conversions of FFA to esters (95–99%) were achieved by treating the greases with 5–20 equiv of methanol at 95 °C for 2 h. The treated greases had a final FFA content of 0.5–1 wt %. We also incorporated these diarylammonium catalysts into insoluble porous polymers via free radical-initiated polymerization. The polymer-immobilized catalysts were found to be equally effective as their homogeneous counterparts in esterifying FFA to esters and were readily recycled and reused for esterification reactions upon reactivation with triflic acid. The resulting ester–glyceride mixtures were then readily converted to total esters by base-catalyzed transesterification. This two-step protocol provides an efficient procedure for the production of biodiesel from greases.

## Introduction

Biodiesel (BD) is defined as the simple fatty acid esters (typically methyl and ethyl) derived from vegetable oils, animal fats, and waste greases. BD is a biodegradable and environmentally benign alternative fuel that is used in diesel engines and heating systems. BD also reduces carbon monoxide and hydrocarbon particulates from diesel engine emissions.<sup>1</sup> In contrast to fossil fuels, BD does not significantly contribute to a net increase in carbon dioxide because for the most part the fatty acids sources from which it is made are photosynthetically derived.<sup>2</sup> In comparison to fuel ethanol, BD production results in a lower release of nitrogen, phosphorus, and pesticide pollutants per net energy gain and is estimated to have a higher energy yield.<sup>1</sup>

Typically, the triglycerides (TG) in the feedstock are directly transesterified with methanol in the presence of an acid, base, or enzyme (lipase) catalyst to afford fatty acid methyl esters (FAME) and glycerol.<sup>3</sup> Currently, the most common commercial process for BD production is by base-catalyzed transesterifi-

cation of a refined vegetable oil with methanol. The vegetable oil feedstock is estimated to account for ~75% of the final BD cost,<sup>4</sup> which presently makes BD economically uncompetitive with petrodiesel. To improve its economic competitiveness, one approach is to use less-expensive feedstocks such as waste-cooking oils or greases for the production of BD.<sup>5</sup>

Greases typically are composed of TG, diglycerides (DG), monoglycerides (MG), and free fatty acids (FFA) (8–40 wt %). A grease containing (8–12 wt % FFA) is categorized as a yellow grease, and a grease containing (>35 wt % FFA) is categorized as a brown grease.<sup>6</sup> Yellow and brown greases are used as animal feeds, but this practice has been curtailed with the advent of mad cow disease in North America and Europe. As a result, there are mandates that all greases be properly disposed of or used in ways that pose no danger to human or animal health.<sup>7</sup> One approach to their use is to convert such greases to biodiesel fuels. The FFA in greases, however, present a major problem when using a base-catalyzed transesterification process since the FFA react with the base catalyst to form soaps, which leads to loss of catalyst and ester product, and increases in production processing costs.<sup>8,9</sup> In 2001, Canakci et al.<sup>10</sup> reported that grease feedstocks could be used for BD production after an acid

<sup>†</sup> Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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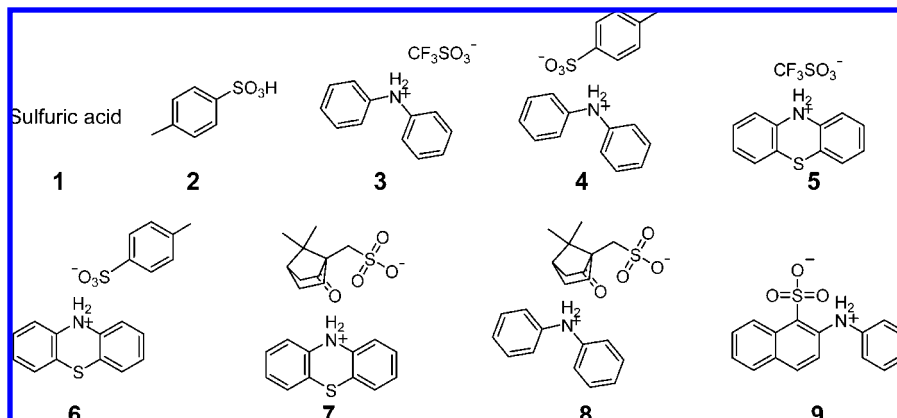
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**Figure 1.** Chemical structures of the homogeneous catalysts used in this work.

pretreatment step that reduced the FFA content in the greases to <1 wt %. They first esterified the FFA to FAME with methanol using sulfuric acid (**1**) as the catalyst. The pretreated greases were then subjected to base-catalyzed transesterification reactions to afford FAME and glycerol. A large amount of base was required, however, to neutralize the acid catalyst remaining in the pretreated greases using this two-step process, which increases the production cost of BD from greases. Other acid catalysts including HCl, BF<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> also were examined, but they did not work as well as sulfuric acid.<sup>11</sup> There thus is a need to develop efficient catalysts that can reduce the FFA content in greases (<1 wt %) and that can be easily removed from the treated greases.

A recent report by Tanabe et al. showed that diphenylammonium triflate and its derivatives catalyze the esterification of carboxylic acids with sterically hindered alcohols in high yields.<sup>12</sup> In this paper, we examined the use of such diarylammonium salts as catalysts for converting the FFA in greases to FAME. The homogeneous diarylammonium catalysts were shown to be highly efficient in reducing the FFA content of the grease to 0.5–1 wt %. We also incorporated these diarylammonium catalysts into insoluble porous polymers via free radical initiated polymerization and demonstrated that the immobilized diarylammonium catalysts are as effective as their homogeneous counterparts in esterifying the FFA in greases. Once the FFA content of the greases was reduced to <1 wt %, the heterogeneous catalysts were removed by centrifugation and the greases were then subjected to base-catalyzed transesterification.<sup>13,14</sup> The work demonstrates the utility of diarylammonium catalysts in reducing the FFA content in greases and represents a promising alternative approach for the production of biodiesel from FFA containing feedstocks. A preliminary account of this work has recently been published.<sup>15</sup>

## Experimental Section

**Materials.** Oleic acid (90%), methanol, diphenylamine, aniline, and triflic acid (TfOH) were purchased from Aldrich Chemical (Milwaukee, WI). Sodium methylate solution was from Degussa

Corporation (Parsippany, NJ). 4-Bromostyrene was purchased from Alfa Aesar (Ward Hill, MA). All other reagents used were of the highest purity available from commercial suppliers. The mixed yellow (12% FFA) and brown greases (**21** and 40% FFA) used in this study were from Kaluzny Bros. Inc. (Joliet, IL) and Darling International Inc. (Irving, TX), respectively.

**Synthesis and Characterization of Diarylammonium Compounds.** The general procedure was as follows: The sulfonic acid (10 mmol) was added to a solution of the arylamine (10 mmol) in toluene (~20 mL) at room temperature (rt) under a nitrogen flow. The reaction mixture was stirred for 15 min, and the precipitated solid was filtered and washed with hexane (~125 mL) to give the arylammonium sulfonate salts (Figure 1) in >90% yield. The detailed spectroscopic data for **3–9** are listed in the Supporting Information.

**Synthesis of Heterogeneous Catalysts. Porous 1,4-Divinylbenzene/4-Bromostyrene (Poly DVB/BrPh) Copolymer.** A 20 mL thick-walled pressure vial equipped with a magnetic stir bar and septum was charged with 2,2'-azobis(2-methylpropionitrile) (AIBN, 44.2 mg, 0.27 mmol), 1,4-divinylbenzene (DVB, 2.58 mL, 2.36 g, 18.1 mmol), 4-bromostyrene (0.42 mL, 0.59 g, 3.2 mmol), and toluene (3.0 mL, 1:1 total monomer volume). The stirred mixture was degassed and purged with argon gas three times. The septum was replaced with a screw cap, and the vial was immersed in an oil bath at 80 °C for 12 h. The solidified mixture was dried in vacuo for 6 h. The solid polymer was ground and purified by Soxhlet extraction with methanol for 24 h. The polymer resin was dried in vacuo to give a white solid with a loading of 1.1 mmol BrPh/g polymer.

**Porous 1,4-Divinylbenzene/Phenyl(vinylaniline) (Poly DVB/PVA-1) Copolymer.** In a glovebox, a 25 mL thick-walled pressure vial equipped with a silicone seal cap was charged with the above Poly DVB/BrPh copolymer (1.46 g, 1.61 mmol BrPh), tris(dibenzylideneacetone)-dipalladium (Pd<sub>2</sub>dba<sub>3</sub>, 14.8 mg, 0.016 mmol), racemic-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (*rac*BINAP, 30.1 mg, 0.048 mmol), and NaO<sup>t</sup>Bu (0.223 g, 2.25 mmol).<sup>16</sup> Aniline (0.15 mL, 1.61 mmol) and distilled toluene (4.0 mL) were added by syringe to the sealed vial, and the mixture was sonicated for 30 min. The reaction vessel was microwaved under the following conditions: power, 300 W; pressure, 100 psi; temperature, 140 °C; reaction time, 25 min. After the mixture was cooled, the contents were centrifuged, the organic layer was decanted, and the solid residue was sonicated with THF (10 mL) for 30 min. After centrifugation, THF was decanted and a mixture of triethylamine/THF 1:1 (10 mL) was added. After stirring for 30 min, the mixture was centrifuged and the solvents removed to afford 1.51 g of porous Poly DVB/PVA-1 copolymer.

**Porous 4-Divinylbenzene/Phenyl(vinylanilinium) Triflate Copolymer, **10**.** Poly DVB/PVA-1 polymer (0.75 g) was treated with 14.3 mL of a 0.4 M solution of triflic acid in 10% 1,4-dioxane in

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dichloromethane (10 equiv) at rt for 6 h. The mixture was centrifuged, and the remaining solid was rinsed and centrifuged five times with EtOAc (10 mL) and then dried in vacuo to afford 0.80 g of **10** as a pale brown solid (1.0 mmol/g loading).

*N*-Phenyl-4-vinylaniline. In a glovebox, a 10 mL thick-walled pressure vial equipped with a silicone seal cap was charged with NaO<sup>t</sup>Bu (0.694 g, 7.00 mmol), Pd(OAc)<sub>2</sub> (22.5 mg, 0.10 mmol), and *rac*BINAP (124.5 mg, 0.20 mmol). Aniline (0.46 mL, 5.0 mmol), 4-bromostyrene (0.65 mL, 5.0 mmol), and distilled toluene (5 mL) were added via a syringe, and the mixture was sonicated for 30 min. The reaction vessel was then microwaved under the following conditions: power, 300 W; pressure, 100 psi; temperature, 140 °C; reaction time, 25 min. The color of the reaction mixture changed from red to dark brown. The mixture was diluted with ethyl acetate and filtered. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica using hexane and 50:1 hexane:EtOAc to give the desired product as a pale yellow solid.

*tert*-Butyl Phenyl(4-vinylphenyl)carbamate. A 25 mL round-bottom two-neck flask equipped with a magnetic stir bar and a reflux condenser was flame-dried and charged with *N*-phenyl-4-vinylaniline (218.3 mg, 1.12 mmol), di-*tert*-butyl dicarbonate (Boc<sub>2</sub>O, 378.0 mg, 1.68 mmol), and 4-(dimethylamino)pyridine (DMAP, 13.6 mg, 0.11 mmol). Anhydrous acetonitrile (1 mL) was added, and the mixture stirred at reflux for 24 h. After the reaction mixture cooled to rt, water was added (25 mL). The product was extracted with EtOAc (30 mL) three times, and the combined organic layers were washed three times with water (20 mL), dried over MgSO<sub>4</sub>, and filtered. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica using hexane and 50:1 hexane:EtOAc to give the desired product as a pale yellow solid (186.2 mg, 56.3%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.4–7.1 (m, 8H), 6.90 (t, 1H), 6.65 (q, 1H), 5.68 (d, 1H), 5.20 (d, 1H), 1.42 (s, 9H). MS *m/z* = 295.2 ([M<sup>+</sup>]).

*Boc*-Protected Porous 1,4-Divinylbenzene/Phenyl(vinylaniline) (Poly DVB/DVA-2-Boc) Copolymer. A 20 mL screw-capped glass vial equipped with a magnetic stir bar and septum was charged with AIBN (11.3 mg, 0.069 mmol), DVB (0.66 mL, 0.60 g, 4.61 mmol) and *tert*-butyl phenyl(4-vinylphenyl)carbamate (0.15 g, 0.508 mmol), and toluene (0.7 mL, 1:1 total monomer volume). The mixture was degassed and purged three times with argon gas, the septum was replaced with a screw cap, and the vial was immersed in an oil bath at 80 °C for 12 h. Then, the solidified reaction mixture was dried in vacuo for 6 h. The solid polymer was ground and purified by Soxhlet extraction with methanol for 24 h. The residue was dried in vacuo to give a white solid of Poly DVB/DVA-2-Boc (0.74 g, 0.68 mmol/g loading).

Porous 1,4-Divinylbenzene (DVB)/Phenyl(vinylaniline) Triflate Copolymer, **11**. Poly DVB/DVA-2-Boc (0.70 g, 0.48 mmol) was treated with 20 mL of 0.125 M triflic acid in 10% 1,4-dioxane in dichloromethane (5 equiv) for simultaneous deprotection and amine protonation. The mixture was allowed to stir at rt for 6 h and then centrifuged. After rinsing with EtOAc (20 mL, 5 times) and centrifuging, the residue was dried in vacuo to afford **11** as a dark brown solid (0.73 g, 0.68 mmol/g loading).

2,6-Dimethyl-*N*-(4-vinylphenyl)aniline, 3,5-Dimethyl-*N*-(4-vinylphenyl)aniline, 2,4,6-Trimethyl-*N*-(4-vinylphenyl)aniline, and 2,6-Difluoro-*N*-(4-vinylphenyl)aniline. These compounds were prepared similarly to *N*-phenyl-4-vinylaniline. Their detailed synthesis and characterization data can be found in the Supporting Information.

Porous 1,4-Divinylbenzene/2,6-Dimethyl-*N*-(4-vinylphenyl)aniline (Poly DVB/2,6-PVA) Copolymer. A 20 mL scintillation vial equipped with a magnetic stir bar and a septum was charged with AIBN (12.7 mg, 0.077 mmol), 1,4-divinylbenzene (DVB) (0.74 mL, 0.68 g, 5.20 mmol), 2,6-dimethyl-*N*-(4-vinylphenyl)aniline (0.169 g, 0.759 mmol), and toluene (0.8 mL, 1:1 total monomer volume). The mixture was degassed and purged three times with argon gas. The septum was replaced with a screw cap, and the vial was immersed into an oil bath at 80 °C for 12 h with stirring. The reaction mixture had solidified and was dried in vacuo for 6 h. The solid polymer was ground and purified via Soxhlet extraction

with methanol as the solvent for 24 h. The residue was dried in vacuo to give a white solid of Poly DVB/2,6-PVA (0.888 g, 0.90 mmol/g).

Porous 1,4-Divinylbenzene/3,5-Dimethyl-*N*-(4-vinylphenyl)aniline (Poly DVB/3,5-PVA) Copolymer. A 20 mL scintillation vial equipped with a magnetic stir bar and a septum was charged with AIBN (12.5 mg, 0.073 mmol), DVB (0.73 mL, 0.67 g, 5.13 mmol), 3,5-dimethyl-*N*-(4-vinylphenyl)aniline (0.167 g, 0.748 mmol), and toluene (0.8 mL, 1:1 total monomer volume). The mixture was degassed and purged three times with argon gas. The septum was replaced with a screw cap, and the vial was immersed into oil bath at 80 °C for 12 h with stirring. The reaction mixture had solidified and was dried in vacuo for 6 h. The solid polymer was ground and purified via Soxhlet extraction with methanol as the solvent for 24 h. The residue was dried in vacuo to give a white solid of Poly DVB/3,5-PVA (0.891 g, 0.90 mmol/g).

Porous 1,4-Divinylbenzene/2,4,6-Trimethyl-*N*-(4-vinylphenyl)aniline (Poly DVB/2,4,6-PVA) Copolymer. A 20 mL scintillation vial equipped with a magnetic stir bar and a septum was charged with AIBN (14.9 mg, 0.091 mmol), DVB (0.87 mL, 0.79 g, 6.09 mmol), 2,4,6-trimethyl-*N*-(4-vinylphenyl)aniline (0.198 g, 0.836 mmol), and toluene (0.8 mL, 1:1 total monomer volume). The mixture was degassed and purged three times with argon gas. The septum was replaced with a screw cap, and the vial was immersed into oil bath at 80 °C for 12 h with stirring. The reaction mixture had solidified and was dried in vacuo for 6 h. The solid polymer was ground and purified via Soxhlet extraction with methanol as solvent for 24 h. The residue was dried in vacuo to give a white solid of Poly DVB/2,4,6-PVA (0.990 g, 0.84 mmol/g).

Porous 1,4-Divinylbenzene/2,6-Difluoro-*N*-(4-vinylphenyl)aniline (Poly DVB/2,6-2F-PVA) Copolymer. A 20 mL scintillation vial equipped with a magnetic stir bar and a septum was charged with AIBN (24.8 mg, 0.151 mmol), DVB (1.44 mL, 1.32 g, 10.13 mmol), 2,6-difluoro-*N*-(4-vinylphenyl)aniline (0.330 g, 1.415 mmol), and toluene (1.5 mL, 1:1 total monomer volume). The mixture was degassed and purged three times with argon gas. The septum was replaced with a screw cap, and the vial was immersed into an oil bath at 80 °C for 12 h with stirring. The reaction mixture had solidified and was dried in vacuo for 6 h. The solid polymer was ground and purified via Soxhlet extraction with methanol as the solvent for 24 h. The residue was dried in vacuo to give a white solid of Poly DVB/2F-PVA (1.65 g, 0.857 mmol/g).

Activation of Porous Polymers To Generate Poly DVB/PVA-OTf Analogs (**11**–**14**). The above polymers were activated in a similar fashion as **10** by treating with 15 mL of 0.23 M solution of triflic acid in 10% 1,4-dioxane in dichloromethane (5 equiv). The mixture was allowed to stir at rt for 6 h and then centrifuged. The solid was rinsed and centrifuged with EtOAc (5 × 20 mL) and then dried in vacuo to afford the activated polymer.

**Catalytic Reactions. Esterification of Oleic Acid.** Oleic acid (90%, 100 mg, 0.35 mmol), methanol (230 mg, 7.1 mmol), and diphenylammonium triflate (1.1 mg, 3.5 μmol) were mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2 h. The reaction mixture went from colorless to a dark red color. The mixture was allowed to cool to rt and ~5 mL of hexane was added to transfer the mixture into a 25 mL one-neck round-bottom flask. The solvents were evaporated under reduced pressure, and the crude product was analyzed by GC and HPLC.

**Esterification of Free Fatty Acid in Greases using Homogeneous Catalyst.** Grease (12 wt % FFA, 1g, 0.43 mmol based on the FFA content), methanol (0.18 g, 5.6 mmol), and diphenylammonium triflate (1.8 mg, 5.8 μmol) were mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2 h. The reaction went from light yellow to a dark brown color. The mixture was allowed to cool to rt and transferred with hexane (~5 mL) into a 25 mL one-neck round-bottom flask. The solvents were evaporated under reduced pressure. A 10 μL portion of crude product was pipetted into a 2 mL vial, and ~1.5 mL of hexane was added. The mixture was passed through a syringe filter and analyzed by HPLC.



**Esterification of Free Fatty Acid in Greases with Heterogeneous Catalysts.** Grease (12 wt % FFA, 5g, 2.1 mmol based on the FFA content), methanol (1.4 g, 0.043 mol), and **11** (0.68 mmol/g, 78 mg, 0.053 mmol) were mixed in a 25 mL three-neck round-bottom flask equipped with a thermometer and a reflux condenser. The reaction mixture was placed into a mineral oil bath set at 95 °C (90 °C internal temperature) for 2 h. The reaction turned from light yellow to a dark brown color. The mixture was cooled to rt and an aliquot (~10 µL) of the product was taken for HPLC analysis.

The esterification reaction was also carried out in the same fashion as above in a 50 g scale with a 600 mL high pressure stainless steel vessel (Parr Instrument, Moline, IL) equipped with a mechanical stirrer and an electric heating mantle equipped with a temperature controller. The vessel was sealed and purged with 40 psi N<sub>2</sub> (3 × for 15 min each). The N<sub>2</sub> gas in the reactor was removed, and the mixture was heated to 95 °C for ~2 h. The mixture was cooled to rt, and the product was analyzed by HPLC.

The crude transesterified product was isolated in one of three ways. In method A, the crude product was vacuum-filtered to remove the solid catalysts from the lipid mixture. Hexane (~10 mL) was added to wash the excess lipids from the solid catalyst, and the mixture was transferred to a 50 mL one-neck round-bottom flask. The solvent was removed under reduced pressure, and the residue (dark brown viscous liquid) was dried under vacuum at rt for ~1 h. The brown liquid product was ready for subsequent reactions. In method B, the crude mixture and the solid catalyst were pipetted into a 25 mL test tube. The test tube was capped tightly and centrifuged at 3000 rpm for 45 min. The liquid mixture was carefully decanted to a second test tube and centrifuged, and the clear supernatant was used for subsequent reactions. Method C was similar to method B except that after the centrifugation step, to remove the solid catalysts, the reaction mixture was then transferred into a 125 mL separatory funnel where the lipid mixture and the methanol/water layer were separated. The lipid mixture settled to the bottom and was drained off for subsequent reaction.

**Transesterification of Pretreated Greases.** The oil phase, [250 mg, 0.28 mmol (<1 wt % FFA) relative to equivalent moles of FFA in pretreated greases], methanol (180 mg, 5.6 mmol), and 5.5 N sodium methoxide in methanol (2.5 µL, 0.3 wt %, relative to the equivalent moles of FFA in pretreated greases) were mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 50 °C for ~2 h. The reaction mixture went from brown to light yellow in color. The mixture was allowed to cool to rt, and two phases were observed. The mixture was transferred with hexane into a 60 mL separatory funnel, and ~5 mL of 1 N HCl was added to the mixture to neutralize the base. The hexane layer was washed with water (~30 mL, 2 times) and dried with MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. The light yellow liquid product was analyzed by HPLC.

**Catalyst Reuse Experiments.** Catalyst **11** (100 mg) recovered from the above experiment was used in the catalyst reuse experiments. The residual dark brown solid catalyst was treated with 5 equiv of 0.1 M TfOH in dioxane (~3.9 mL) at rt for ~20 h. The solid was centrifuged, washed with dioxane (5 × 8 mL), and dried under vacuum for ~20 h at rt. The freshly reactivated catalyst, yellow grease (12 wt % FFA), and methanol were then recharged for a subsequent esterification reaction. This process was repeated for subsequent reuse cycles.

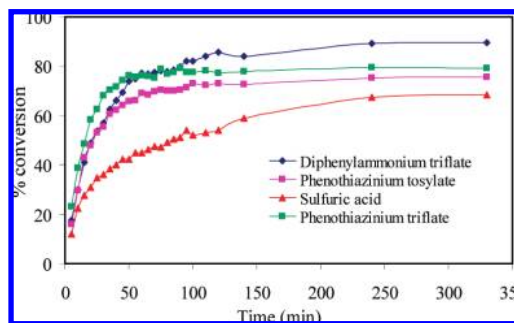
## Results and Discussion

**Esterification of Oleic Acid using Diarylammonium Catalysts.** A series of arylammonium salts **3–9** (Figure 1) was synthesized and tested as catalysts for the esterification of oleic acid with methanol. The synthesized catalysts were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and their melting points were determined. As shown in Table 1, oleic acid was effectively esterified in the presence of the arylammonium catalysts to afford methyl oleate. In general, the ammonium triflate salts **3**

**Table 1. Esterification of Oleic Acid with Homogeneous Catalysts<sup>a</sup>**

entry	catalyst (0.5 mol % loading)	HPLC wt %	
		methyl oleate	oleic acid
1	H <sub>2</sub> SO <sub>4</sub> ( <b>1</b> )	65	35
2	<i>p</i> -toluenesulphonic acid ( <b>2</b> )	81	19
3	diphenylammonium triflate ( <b>3</b> )	99	1.0
4	diphenylammonium tosylate ( <b>4</b> )	93	7.0
5	phenothiazinium triflate ( <b>5</b> )	98	2.0
6	phenothiazinium tosylate ( <b>6</b> )	80	20
7	phenothiazine camphorsulfonate ( <b>7</b> )	77	23
8	diphenylammonium camphorsulfonate ( <b>8</b> )	87	13
9	2-phenylamino-naphthalene-1-sulfonic acid ( <b>9</b> )	5.0	95

<sup>a</sup> All reactions were performed with oleic acid (90% purity) and 2 equiv of MeOH at 95 °C for 2 h.



**Figure 2.** Oleic acid to methyl oleate conversion curves for different catalysts at 1 mol % loadings. All of the reactions were performed with 1:1 molar ratio of oleic acid and MeOH at 75 °C.

and **5** (Table 1) appeared to be the more active catalysts; at a 0.5 mol % loading of **3** and **5**, oleic acid was esterified to methyl oleate >98% conversion with 2 equiv of methanol at 95 °C in 2 h. On the other hand, the diarylammonium *p*-toluene sulfonate salts were less effective esterification catalysts. For example, under identical conditions as above diphenylammonium tosylate (**4**) and phenothiazine tosylate (**6**) gave conversions of 93% and 80%, respectively. We also examined other types of arylammonium compounds such as phenothiazinium camphorsulfonate (**7**), diphenylammonium camphorsulfonate (**8**), and 2-phenylamino-naphthalene-1-sulfonic acid (**9**). Oleic acid conversions to methyl oleate with catalysts **7** and **8** were only 77%, 87%, respectively, while **9** was ineffective. This conversion trend is consistent with that of the acidities of the catalysts.

For comparison, we also carried out control esterification experiments using sulfuric (**1**) and *p*-toluenesulphonic acid (**2**) as catalysts under the same conditions, obtaining 65% and 81% conversions, respectively. It was thus encouraging to find that the arylammonium catalysts **3–6** gave significantly higher esterification conversions than acids more commonly used as esterification catalysts.

Figure 2 shows the oleic acid to methyl oleate conversion curves when using the arylammonium catalysts **3**, **5**, and **6** versus sulfuric acid. Since the arylammonium tosylate compounds did not work as well as their triflate counterparts, we only examined the conversion profile for catalyst **6**, which gave the best yields for this catalyst type (Table 1). The reactions were performed with 1 mol % catalyst and 1 equiv methanol at 75 °C. Aliquots of the reactions were sampled to determine the percent conversion every 5 min over the first 2 h of reaction and hourly thereafter. Figure 2 shows that the arylammonium catalysts are highly active but the percent conversions varied with catalyst type. After 5.5 h of reactions, catalysts **1**, **3**, **5**, and **6** gave a conversion of 68.5%, 89.6%, 79.1%, and 75.5%,

**Table 2. Esterification of the FFA in Greases (12 wt % FFA) to FAME Using Homogeneous Catalysts<sup>a</sup>**

entry	catalyst (mol % loading)	MeOH (equiv) <sup>c</sup>	HPLC wt %					% conv of FFA <sup>d</sup>
			FAME	FFA	TG	DG	MG	
1	no catalyst		0	12	66.0	20.4	1.6	
2	<b>1</b> (2.5)	10	18.3	0.9	54.8	22.4	3.6	93
3	<b>3</b> (2)	10	17.9	1.2	56.7	20.8	3.4	90
4	<b>5</b> (2)	20	17.2	1.1	59.4	19.6	2.7	91
5	<b>6</b> (2) <sup>b</sup>	20	14.7	0.4	61.7	21.6	1.6	97
6	<b>3</b> (2.5)	10	20.1	0.7	55.7	19.4	4.1	94
7	<b>4</b> (2.5) <sup>b</sup>	20	3.20	14	56.2	22.6	4.0	0
8	<b>5</b> (2.5)	20	17.3	0.9	60.4	19.1	2.3	93
9	<b>5</b> (3)	5	21.0	1.0	52.9	21.6	3.5	92
10	<b>6</b> (3) <sup>b</sup>	20	17.4	0	59.5	20.4	2.7	>99

<sup>a</sup> All reactions were performed at 95 °C for 2 h. <sup>b</sup> Grease was filtered with Celite before use. <sup>c</sup> Number of equivalents relative to the FFA that is present in greases. <sup>d</sup> Percent conversion =  $100 \times (\text{FFA}^i - \text{FFA}^f) / \text{FFA}^i$ ; where  $\text{FFA}^i$  = initial wt % FFA in the grease and  $\text{FFA}^f$  = final wt % FFA in the esterified grease.

respectively. The activities can be grouped in the following order: diphenylammonium triflate > phenothiazinium triflate > phenothiazinium tosylate > H<sub>2</sub>SO<sub>4</sub>. The arylammonium catalysts thus not only give higher conversions but also are more active than sulfuric acid.

**Homogeneous Diarylammonium-Catalyzed Esterification of FFA in Greases.** Esterification experiments were carried out with greases containing 12, 21, and 40 wt % FFA. The reactions were run with different catalysts at various loadings and molar ratios of methanol to FFA in the grease. As shown in Table 2, for grease containing 12 wt % FFA, catalysts **3–6** gave a conversion of FFA to FAME between 90–99% after a reaction time of 2 h at 95 °C. The conversion obtained with the ammonium catalysts is comparable to those obtained using sulfuric acid under similar conditions (Table 2). A catalyst loading of 2–3 mol % was needed to reduce the FFA content down to an acceptable level (<1 wt %). For example, using 10 equiv of methanol and a 2 and 2.5 mol % catalyst loading of **3** resulted in an FFA conversion to FAME of 90% and 94% (with 1.2% and 0.73% FFA remaining), respectively (entries 3 and 6 in Table 2). As shown in Table 2, there also were minor changes in the glyceride composition of the grease when using these catalysts under the esterification conditions used in this study.

Triflate catalyst **5** (Table 2) also reduced the FFA content of the grease to ~1 wt % when a 2.5–3 mol % catalyst loading was used. With 20 equiv of methanol, 2 mol % and 2.5 mol % of **5** gave an FFA conversion to FAME of 91% and 93% (with 1.1% and 0.85% FFA remaining), respectively. At 3 mol % loading, **5** gave an FFA conversion of 92% FAME when only 5 equiv of methanol was used (entry 9, Table 2). For the tosylate complexes **4** and **6** (entries 5 and 7), the greases needed to be filtered with Celite before use to remove unknown impurities that inhibited esterification. As shown in Table 2, in the presence of 20 equiv of methanol and 2 and 3 mol % of catalyst **6** (entries 5 and 10), a conversion of FFA to FAME of 96% and >99%, respectively, was observed. Catalyst **4** (entry 7) did not work well under similar conditions in that the conversion of FFA to FAME was only 35%.

We also examined the esterification of FFA to FAME in grease that contained 21 wt % FFA using catalysts **1**, **3**, and **6**. The FFA content in the untreated grease could be reduced to <1 wt % with the arylammonium catalysts. As shown in Table 3, catalyst **3** worked the best for the esterification of FFA to FAME in this grease. At 2.5 mol % of catalyst **3**, an FFA conversion to FAME of 94% was obtained using 10 equiv of methanol, while with 3 mol % of catalyst **3** and 5 equiv of

**Table 3. Esterification of FFA in Greases (21 wt % FFA) to FAME using Homogeneous Catalysts<sup>a</sup>**

entry	catalysts (mol % loading)	MeOH (equiv) <sup>b</sup>	HPLC wt %					% conv of FFA <sup>c</sup>
			FAME	FFA	TG	DG	MG	
1	no catalyst		0	21.4	40.3	30.2	8.9	
2	<b>1</b> (2.5)	10	28.5	2.19	35	27.8	6.5	90
3	<b>1</b> (3)	10	28.3	1.94	34.2	29.3	6.3	91
4	<b>3</b> (2.5)	10	32.3	1.3	32.3	23.9	10	94
5	<b>4</b> (2.5)	10	2.0	22.6	33.9	34.2	7.3	
6	<b>5</b> (2.5)	10	25	2.47	37.6	28.9	6.1	88
7	<b>6</b> (2.5)	10	6.0	18	40	31.2	4.8	16
8	<b>3</b> (3)	5	25.6	1.8	36.6	27.8	8.2	92
9	<b>4</b> (3)	20	6.35	25.1	32.7	29.7	5.6	
10	<b>5</b> (3)	10	33.4	1.3	31.9	24.3	9.1	94
11	<b>6</b> (3)	10	20.1	4.9	38.5	29.9	6.6	77

<sup>a</sup> All reactions were performed at 95 °C for 2 h. <sup>b</sup> Number of equivalents relative to the FFA that is present in greases. <sup>c</sup> Percent conversion =  $100 \times (\text{FFA}^i - \text{FFA}^f) / \text{FFA}^i$ ; where  $\text{FFA}^i$  = initial wt % FFA in the grease and  $\text{FFA}^f$  = final wt % FFA in the esterified grease.

**Table 4. Esterification of FFA Greases (40 wt % FFA) with Various Homogeneous Catalysts<sup>a</sup>**

entry	catalysts (mol % loading)	MeOH (equiv) <sup>b</sup>	HPLC wt %					% conv of FFA <sup>c</sup>
			FAME	FFA	TG	DG	MG	
1	no catalyst		0	40	31.6	25	3.4	
2	<b>1</b> (3)	20	49.1	1.0	17.5	24.6	7.8	98
3	<b>3</b> (3)	20	44.8	0.7	28.6	22.1	3.8	98
4	<b>4</b> (3)	20	42.9	2.0	25.7	23.2	6.2	95
5	<b>5</b> (3)	20	45.1	0.8	28.3	22.0	3.8	98
6	<b>6</b> (3)	20	45.2	1.5	22.2	23.6	7.44	96

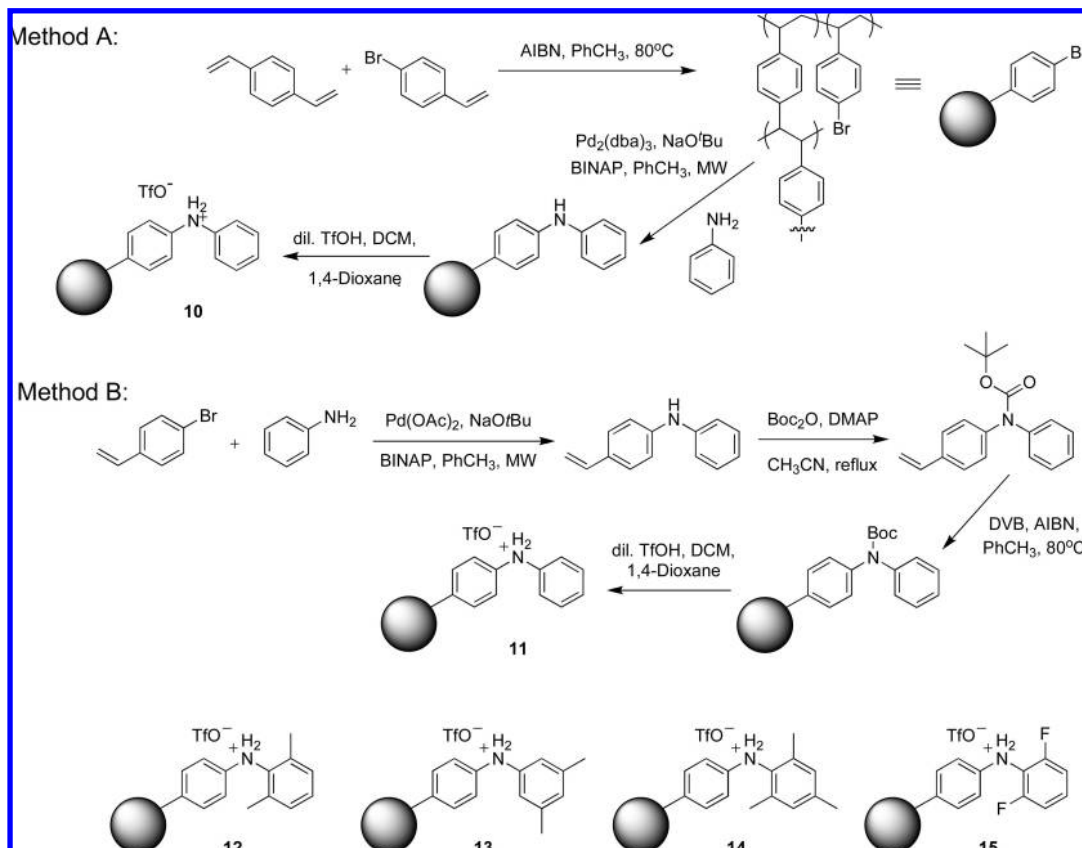
<sup>a</sup> All reactions were performed at 95 °C for 2 h, and the grease was filtered with Celite before use. <sup>b</sup> Number of equivalents relative to the FFA that is present in greases. <sup>c</sup> Percent conversion =  $100 \times (\text{FFA}^i - \text{FFA}^f) / \text{FFA}^i$ ; where  $\text{FFA}^i$  = initial wt % FFA in the grease and  $\text{FFA}^f$  = final wt % FFA in the esterified grease.

methanol, a 91% conversion of FFA to FAME (entries 4 and 8, Table 3) was found.

When brown grease (40 wt % FFA) was used as a substrate for the esterification process, the grease had to be first filtered through Celite. As shown in Table 4, excellent conversions of FFA to FAME in this substrate were obtained at 3 mol % catalyst loading of **3–6** and 20 equiv of methanol. The arylammonium triflate catalysts reduced the FFA content to <1 wt %. These results clearly show the utility of arylammonium salts in catalyzing the conversion of FFA to FAME in greases with high FFA content.

**Synthesis of Porous 1,4-Divinylbenzene/Phenyl(Vinyl-anilinium) Copolymers.** One problem associated with homogeneous catalysts is the difficulty of their recovery and/or reuse after the catalytic reaction. This represents a drawback when homogeneous acid catalysts are used for the pretreatment of greases because the remaining acid catalyst has to be neutralized with base before the reaction mixture can be used in subsequent base-catalyzed transesterification reactions. To overcome this drawback, we immobilized the diarylammonium salts onto porous highly cross-linked organic polymers to prepare potential heterogeneous arylammonium catalysts. An insoluble polymer resin was made by free radical-initiated polymerization of 1,4-divinylbenzene (DVB) with desired comonomers at elevated temperatures in the presence of a porogen.<sup>17</sup> Since the diphenylammonium triflates worked the best for the conversion of FFA to FAME in high FFA containing greases, we focused our attention to the preparation of porous DVB/phenyl(vinyl-anilinium) triflate (DVB/PVA-OTf) copolymers.

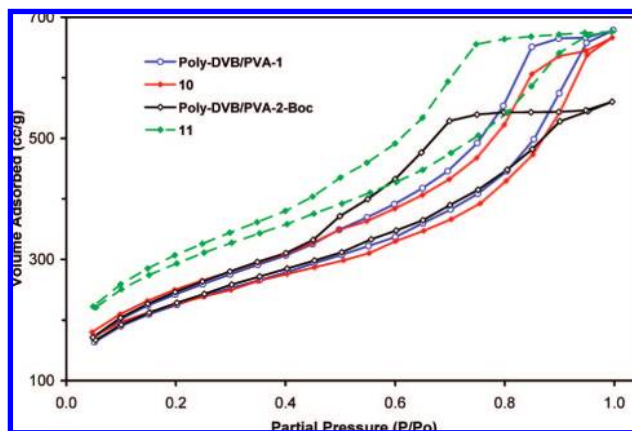
(17) Santora, B. P.; Gagné, M. R.; Moloy, K. G.; Radu, N. S. *Macromolecules* **2001**, *34*, 658–661.



**Figure 3.** Synthetic routes for porous Poly DVB/PVA-OTf copolymers.

We examined two different methods for the synthesis of DVB/PVA-OTf copolymers. In the first approach, we synthesized a porous DVB/4-bromostyrene copolymer (Poly DVB/BrPh), which provided an insoluble platform with accessible bromophenyl moieties (Figure 3). The bromophenyl group was subsequently aminated with aniline under Pd-coupling conditions<sup>18</sup> using a microwave synthesis approach to give a 1,4-divinylbenzene/phenyl(vinylaniline) (Poly DVB/PVA-1) copolymer. After a thorough rinsing of the solid with various solvents and solutions, the polymer now having pendent diphenylamines was reacted with a dilute solution of triflic acid in dichloromethane/1,4-dioxane solvent mixture to afford the heterogeneous catalyst **10** (Figure 3). The resulting solid was dark brown in color, suggesting protonation of the secondary amine. This synthetic scheme relies on the Pd-catalyzed amination reaction to install the phenyl(vinylaniline) moieties, which presents a significant challenge in quantifying the number of active sites in the copolymers since the Pd-coupling reaction efficiency is less than unity.

The second synthetic approach utilized a presynthesized vinyl analogue of diphenylamine as a comonomer in the polymerization with DVB (Figure 3). Because this copolymerization reaction gave a quantitative yield, it is much easier to quantify the number of the diarylammonium active sites in the porous copolymers prepared by the second approach. Pd-catalyzed *N*-arylation of aniline with 4-bromostyrene was performed under microwave reaction conditions to afford *N*-phenyl-4-vinylaniline. This secondary diarylamine, however, inhibits the copolymerization reaction by trapping free radicals. We therefore carried out the copolymerization reaction with the 'Boc-protected' *N*-phenyl-4-vinylaniline. The protected monomer was readily copolymerized with DVB (1:4 molar ratio) to give a quantitative



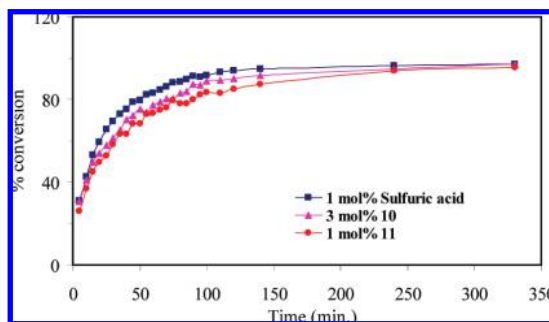
**Figure 4.** Nitrogen sorption isotherms of porous copolymers after 6 h of heating at 100 °C.

yield of Poly DVB/PVA-2. After Soxhlet extraction of the polymer solid with methanol, the resin was treated with dilute triflic acid to simultaneously remove the 'Boc protecting group and protonate the diarylamine to generate the heterogeneous catalyst **11** (Figure 3).

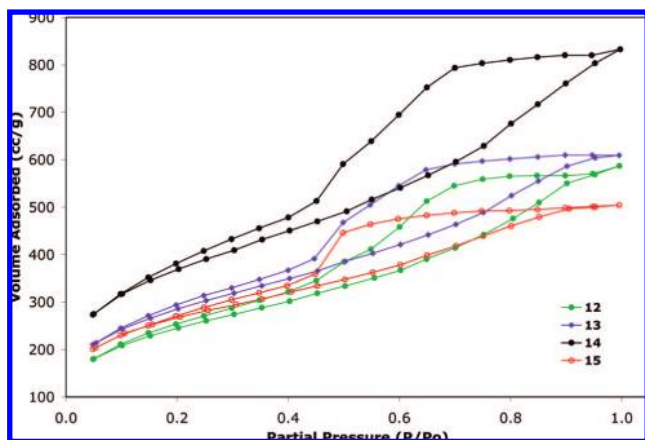
The use of a toluene porogen and rigid diarylamine comonomer allowed the synthesis of highly porous cross-linked copolymers. Nitrogen sorption isotherms on the porous copolymers were measured to estimate their surface area and pore sizes. All of the copolymers exhibited high surface areas (Figure 4). As expected, the surface area slightly decreased from 840 m<sup>2</sup>/g for Poly DVB/BrPh to 730 m<sup>2</sup>/g for **10**, as a result of the increasing steric bulk after the *N*-arylation of Poly DVB/BrPh and subsequent protonation with triflic acid. Interestingly, for the DVB/PVA-OTf copolymers made by the second approach, we observed an increase in surface area as the Poly DVB/PVA-

(18) Weigand, K.; Pelka, S. *Mol. Diversity* **2003**, 7, 181–184.





**Figure 5.** Conversion curves of esterification of oleic acid by solid catalysts. All reactions were performed at an oleic acid:MeOH mol ratio of 1:10 at 95 °C.



**Figure 6.** Nitrogen sorption isotherms for porous copolymers **12**, **13**, **14**, and **15**, heated at 100 °C for 6 h.

**Table 5. Nitrogen Sorption Isotherm Data for Porous Copolymers**

	surface area (m <sup>2</sup> /g)	pore volume (cc/g)
Poly DVB/PVA-1	840	1.03
Poly DVB/PVA-TfOH, <b>10</b>	730	0.97
Poly DVB/PVA-2-Boc	850	0.85
Poly DVB/PVA-TfOH, <b>11</b>	1000	0.99
Poly DVB/2,6-PVA	1241	1.19
Poly DVB/2,6-PVA-TfOH, <b>12</b>	883	0.88
Poly DVB/3,5-PVA	1360	1.20
Poly DVB/3,5-PVA-TfOH, <b>13</b>	977	0.89
Poly DVB/2,4,6-PVA	837	0.78
Poly DVB/2,4,6-PVA-TfOH, <b>14</b>	1278	1.22
Poly DVB/2F-PVA	754	0.64
Poly DVB/2F-PVA-TfOH, <b>15</b>	869	0.71

2-Boc underwent deprotection and protonation steps. Poly DVB/PVA-2-Boc and **11** had surface areas of 850 and 1000 m<sup>2</sup>/g, respectively. This result is consistent with a slightly larger size of the 'Boc protection group over the triflate anion. We have also synthesized several derivatives of the polymer-immobilized diarylammonium triflate **12–15** by AIBN-initiated copolymerization of DVB with substituted *N*-(4-vinylphenyl)aniline. These derivatives did not require Boc protection in order to be copolymerized with DVB. The resulting solids however retained similar porous structures. The nitrogen sorption isotherms showed that these polymers are highly porous with a broad distribution of pore sizes (Figure 6 and Table 5). Given the high porosity and large pore size of the copolymers, the diarylammonium-protonated sites were expected to be readily accessible to the substrates in heterogeneously catalyzed esterification reactions.

**Esterification of the FFA in Greases by Porous Divinylbenzene/Diarylammonium Triflate Copolymers Catalysts.** We first examined the catalytic activity of heterogeneous catalyst **10** for the esterification of oleic acid and FFA in greases. The reactions were carried out under similar conditions to the homogeneous catalyst systems. In the presence of 2 mol % of **10**, an oleic acid to methyl oleate conversion of >99% was obtained when a mixture of oleic acid and 5 equiv of methanol was heated at 95 °C for 2 h (Table 6, entry 1). Solid catalyst **10** also worked well in converting the FFA to FAME in FFA containing greases. In the presence of 7.5 mol % of this catalyst and 20 equiv of methanol, the greases containing 12 and 21 wt % FFA were reduced to 0.45 and 1.1 wt %, respectively (entries 2 and 3). This result corresponds to an FFA conversion to FAME of 96% and 95%, respectively. For brown grease (40 wt % FFA), 15 mol % of **10** gave a >99% conversion of FFA to FAME in the presence of 20 equiv of methanol (entry 4). Since we assumed complete arylation of all the phenyl bromide moieties in Poly DVB/BrPh when calculating catalyst loadings, we apparently overestimated the amount of the PVA-1-OTf active sites and thus underestimated the activity of **10** in all our experiments. We therefore carried out parallel experiments with catalyst **11** to obtain a better estimate of the catalytic activity for the immobilized arylammonium catalysts.

As expected, **11** had a much higher apparent activity than **10**. With only a 0.5 mol % loading of **11**, we were able to completely convert oleic acid to methyl oleate by treatment with 5 equiv of MeOH (Table 6, entry 5). For the grease containing 12 wt % FFA, only 2.5 mol % of **11** was needed to attain a 97% conversion of FFA to FAME (with the final FFA content of 0.41%; entry 6). As for the greases with 21 and 40 wt % FFA, 5 and 7.5 mol % of **11** gave an FFA to FAME conversion of 97% and >99%, respectively (entries 7 and 8). The results indicate that the porous phenyl(vinylanilinium) triflate/divinylbenzene copolymer catalysts are very effective in converting FFA to FAME in greases with high FFA content. These immobilized catalysts also caused change in the glyceride content of the grease much as the homogeneous counterparts, but again, their transesterification activity was low compared to their esterification activity. We also examined time-dependent oleic acid to methyl oleate conversion curves for catalysts **10** and **11**. As shown in Figure 5, both heterogeneous catalysts **10** and **11** have an esterification activity only slightly lower than sulfuric acid.

The derivatives of **11** were synthesized to explore potential electron-donating and withdrawing effects on the acidic nature of the parent diarylammonium triflate. Methylated analogues, **12**, **13**, and **14**, with an anticipated electron-donating effect, all showed a slight decrease in the conversion of oleic acid to methyl oleate (Table 6). When catalysts **13** and **14** were tested on greases containing 12 and 40 wt % FFA, their abilities to convert FFA to FAME was lower than the neat oleic acid to methyl oleate conversion. Surprisingly, **12** reduced the FFA content to ~1.0 wt % for both greases. Catalyst **15** was a much less active esterification catalyst than **11**; with 5 mol % of **15**, an FFA to FAME conversion of 51% was obtained after a 2 h reaction at 95 °C.

**Catalyst Reuse Experiments.** We also demonstrated that catalyst **11** could be recycled and reused for at least three cycles. As shown in Table 7, grease with 12% FFA was used for this study. At 2.5 mol % loading of **11**, 88% of the FFA in this grease was esterified to FAME in the initial reaction. The solid catalyst was recovered by filtration and reactivated with triflic acid. A 92% conversion of FFA to FAME was obtained for the

**Table 6. Esterification of the FFA in Grease Using Heterogeneous Poly DVB/PVA-OTf Catalysts<sup>a</sup>**

entry	substrates	catalyst (mol %)	MeOH (equiv) <sup>b</sup>	HPLC wt %					% conv of FFA <sup>c</sup>
				FAME	FFA	TG	DG	MG	
1	oleic acid (90% purity)	<b>10</b> (2)	5	99	1.0				99
2	grease (12 wt % FFA)	<b>10</b> (7.5)	20	23	0.5	47.9	21.9	6.7	96
3	grease (21 wt % FFA)	<b>10</b> (7.5)	20	24	1.1	32.4	30.5	12	95
4	grease (40 wt % FFA)	<b>10</b> (15)	20	49	0	24.6	21	5.4	>99
5	oleic acid (90% purity)	<b>11</b> (0.5)	5	99	<1.0				>99
6	grease (12 wt % FFA)	<b>11</b> (2.5)	20	20.3	0.4	52.9	22.6	3.8	97
7	grease (12 wt % FFA) <sup>d</sup>	<b>11</b> (2.5)	20	22.4	1.4	54.9	17.3	4.0	88
8	grease (21 wt % FFA)	<b>11</b> (5)	20	29.3	0.7	39.9	24.3	5.8	97
9	grease (40 wt % FFA)	<b>11</b> (5)	20	50.6	1.3	24.5	19.2	4.4	97
10	oleic acid (90% purity)	<b>12</b> (1)	5	84	16				84
11	grease (12 wt % FFA) <sup>e</sup>	<b>12</b> (2.5)	20	16.6	1.1	67.9	12.8	1.6	91
12	grease (40 wt % FFA)	<b>12</b> (5.0)	20	53	1.0	26.1	17.7	2.2	98
13	oleic acid (90% purity)	<b>13</b> (1)	5	97	3				97
14	grease (12 wt % FFA) <sup>e</sup>	<b>13</b> (2.5)	20	17.9	0.7	66.8	13.1	1.5	94
15	grease (40 wt % FFA)	<b>13</b> (5)	20	44.1	6.4	25.4	20.4	3.7	84
16	oleic acid (90% purity)	<b>14</b> (1)	5	99	1				99
17	grease (12 wt % FFA) <sup>e</sup>	<b>14</b> (2.5)	20	10.4	3.1	77	9.5	0	74
18	grease (40 wt % FFA)	<b>14</b> (5)	20	40	8.75	26.5	21.4	3.32	78
19	grease (12 wt % FFA) <sup>e</sup>	<b>15</b> (5)	20	10.3	6.1	75.3	8.3	0	51

<sup>a</sup> All reactions were performed at 95 °C for 2 h. <sup>b</sup> Number of equivalents relative to FFA. <sup>c</sup> Percent conversion =  $100 \times (\text{FFA}^i - \text{FFA}^f) / \text{FFA}^i$ ; where  $\text{FFA}^i$  = initial wt % FFA in the grease and  $\text{FFA}^f$  = final wt % FFA in the esterified grease. <sup>d</sup> Reaction was performed at a 50 g scale in a stainless steel reactor. <sup>e</sup> Weight percent composition of grease before esterification: 12.5 FFA, 79.4 TG, 9.0 DG, 0 MG. Note that since there was only about 6 wt % FFA in the grease obtained from Darling International, we intentionally added another 6 wt % OLA.

**Table 7. Catalyst Reused in Yellow Grease Esterification Reaction<sup>a</sup>**

entry	catalysts <sup>b</sup>	MeOH (equiv) <sup>c</sup>	HPLC wt %					% conv of FFA <sup>d</sup>
			FAME	FFA	TG	DG	MG	
1	no catalyst	0	12	66.0	20.4	1.6		
2	first use	20	22.4	1.4	54.9	17.3	4.0	88
3	second use	20	14.6	1.0	64.6	19.8	0	92
4	third use	20	12.6	1.6	63.2	20.5	2.1	87

<sup>a</sup> All reactions were performed at 95 °C for 2 h with 2.5 mol % catalyst loading. <sup>b</sup> Catalyst **11** was reactivated by treating with 5 equiv of 0.1 M TfOH in dioxane at rt for ~20 h. The catalyst was then washed with dioxane (5 × 8 mL). <sup>c</sup> Number of equivalents relative to FFA. <sup>d</sup> Percent conversion =  $100 \times (\text{FFA}^i - \text{FFA}^f) / \text{FFA}^i$ ; where  $\text{FFA}^i$  = initial wt % FFA in the grease and  $\text{FFA}^f$  = final wt % FFA in the esterified grease.

second reaction again using 2.5 mol % of **11**. In the third run, an 87% conversion of FFA to FAME was achieved under the same conditions with reactivated **11**. These data indicate only minor variations in the esterification activity of **11** after three reaction cycles; however, when the reactivated **11** was used a fourth time under similar reaction conditions, a significant drop in the esterification activity of **11** (~47% conversion of FFA to FAME) was observed.

**Transesterification of Pretreated Greases.** Since the FFA in greases could be converted to FAME with the heterogeneous arylammonium catalysts, it was important to show that the pretreated greases could be directly used for FAME production using well-established base-catalyzed transesterification processes. As seen in Table 8, **11** reduced the FFA content of the grease from 12 (initial) to 0.9 wt % (after pretreatment (entry 1). After the removal of solid catalyst **11** by simple filtration (and removal of volatile solvents), this pretreated grease was subjected to base-catalyzed transesterification. In the presence of 0.3 wt % sodium methoxide ( $\text{NaOCH}_3$ ) catalyst, between 4.4 and 8.5 equiv of methanol (relative to the fatty acyl equivalents in the grease) were needed to completely convert all of the glycerides in the grease to FAME at 50 °C within 2 h. The final mixture contained >98 wt % FAME and less than 2 wt % FFA (entry 4). About half of the residual FFA in the final ester product is carried over from the pretreated grease. It is established that  $\text{NaOCH}_3$  does not catalyze the esterification of FFA to FAME.<sup>19</sup>

**Table 8. Transesterification of Pretreated Greases with 0.3 wt % Sodium Methoxide<sup>a</sup>**

entry	sample	MeOH (equiv) <sup>b</sup>	HPLC wt %				
			FAME	FFA	TG	DG	MG
1	pretreated grease <sup>c</sup>		20.5	0.9	52.4	22.1	4.1
2	after transesterification	3	90.9	1.6	5.5	2.0	0
3	after transesterification	4.4	95.9	1.5	2.6	0	0
4	after transesterification	8.5	98.1	1.9	0	0	0
5	pretreated grease <sup>d</sup>		18.4	0.9	57	20.2	3.4
6	after transesterification	5.8	80.1	1.4	11.8	4.95	1.7
7	after transesterification	7.2	90.6	1.3	6.1	2.0	0
8	after transesterification	11.2	98.6	1.4	0	0	0
9	pretreated grease <sup>d</sup>		22.8	1.8	57.3	14.5	3.6
10	after transesterification	11.7	97.4	2.6	0	0	0
11	pretreated grease <sup>e</sup>		24.2	0.7	54.9	15.7	4.5
12	after transesterification	3	99	1.0	0	0	0

<sup>a</sup> All the transesterification reactions were run with 0.3 wt % NaOMe catalyst at 50 °C for 2 h. <sup>b</sup> Numbers of equiv of MeOH were calculated relative to the equivalent moles of FFA in pretreated greases. <sup>c</sup> The pretreated grease was vacuum-dried to remove water and MeOH from the pretreatment (esterification) step (method A). <sup>d</sup> Catalyst **11** was removed from the pretreated greases by centrifugation, i.e., methanol and water carried over from the esterification step were not removed from the pretreated greases (method B). <sup>e</sup> The esterification reaction of FFA to FAME in grease was performed at a 50 g scale in a 600 mL stainless steel reactor. Catalyst **11** was removed from the pretreated greases by centrifugation, and the mixture was transferred to a separator funnel to separate the lipid mixtures from the methanol/water phase (method C).

We also examined the transesterification reactions using pretreated greases containing residual methanol and water of reaction from the acid-catalyzed pretreatment (esterification) step. In these experiments, the solid catalyst **11** was removed from the pretreated grease by centrifugation. Interestingly, similar results were obtained and the water generated from the pretreatment (esterification) step did not seem to adversely affect the transesterification reactions of the glycerides. For the pretreated grease with 0.95 wt % final FFA content, transesterification with 5.8, 7.2, and 11.2 equiv of MeOH (relative to the fatty acyl equivalents in the grease) in the presence of 0.3

(19) Christie, W. W. *Lipid analysis: Isolation, Separation, Identification, and Structural Analysis of Lipids*; Oily Press: Bridgewater, England, 2003; p 205.



wt % NaOCH<sub>3</sub> gave a final FAME content of 80.1, 90.6, and 98.6 wt %, respectively (Table 8, entries 6–8). The reaction product with 11.2 equiv of MeOH (including the carried-over MeOH) had a final FFA content of 1.43 wt % with no glycerides left in the mixture. The base-catalyzed transesterification reaction also worked well for the pretreated grease containing 1.78 wt % FFA. With 0.3 wt % NaOCH<sub>3</sub> and 11.7 equiv of MeOH (including the carried-over MeOH), the final product contained 97.4 wt % FAME and 2.62 wt % FFA (no remaining glycerides) (Table 8, entry 10). Interestingly, when the lipid mixture was separated from the MeOH/water layer, only 3 equiv of MeOH and 0.3 wt % NaOCH<sub>3</sub> were needed to reduce all of the glycerides in the pretreated grease to 99 wt % FAME (Table 8, entry 12).

### Conclusions

We have successfully synthesized a family of diarylammonium catalysts for the esterification of FFA in greases containing between 12–40% FFA. The catalysts were highly effective for the esterification of FFA in greases, reducing the FFA contents to <1%. We have also incorporated these diarylammonium catalysts into insoluble porous polymers via free radical-initiated

polymerization. The immobilized diphenylammonium triflate catalysts were nearly as effective as their homogeneous counterparts in reducing the FFA content in greases to <1%. The heterogeneous diarylammonium catalysts were readily removed from the treated greases, which were then directly converted to FAME in subsequent base-catalyzed transesterification reactions. This work thus demonstrates the utility of diarylammonium salts as catalysts in reducing the FFA content in greases. The two-step process represents a promising alternative approach for the production of BD from feedstocks containing high amounts of FFA.

**Acknowledgment.** We thank Mr. Kerby Jones for assistance with the HPLC analyses and Mr. Justin Miller for assisting with experimental portions of the work. We also would like to acknowledge Dr. Michael J. Haas for his critical reading of the manuscript.

**Supporting Information Available:** Experimental details and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

EF700343B